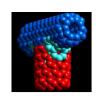
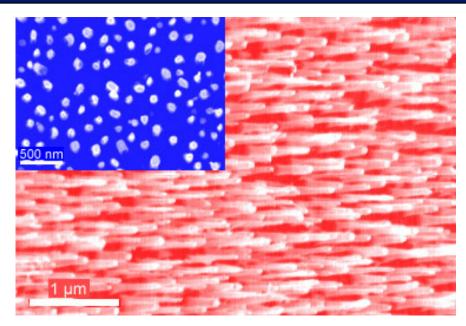


### Nanotechnology: Opportunities and Challenges

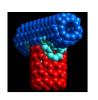




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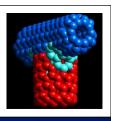
## **Agenda**

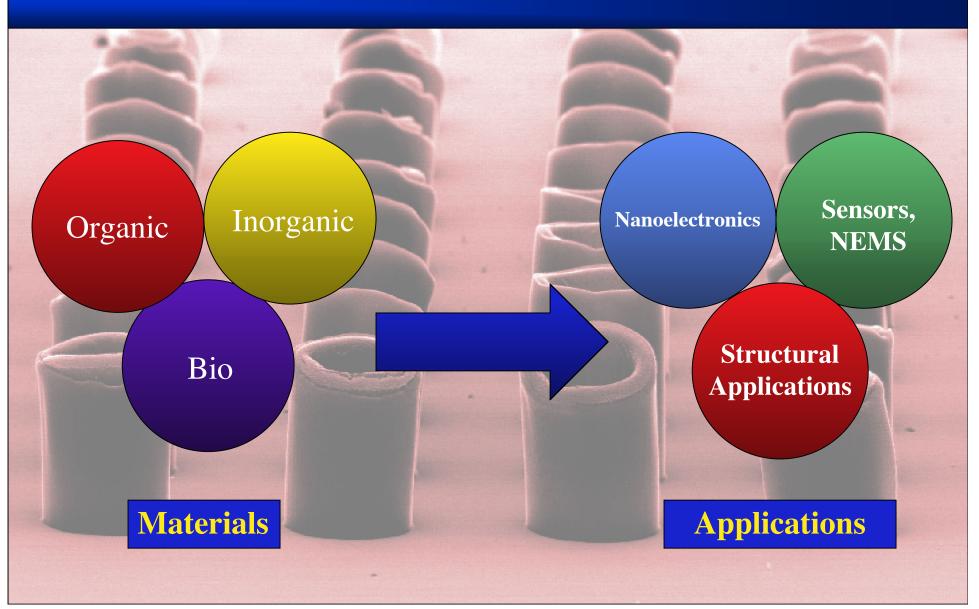


- Impact of Nanotechnology on various sectors
- National Nanotechnology Initiative
- Carbon Nanotubes
  - CNT growth and characterization
  - CNT based microscopy
  - CNT based biosensors
- Some other Nano examples
- Educational Issues



## Nanotechnology R & D







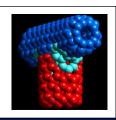
### Some Fundamental Science Issues

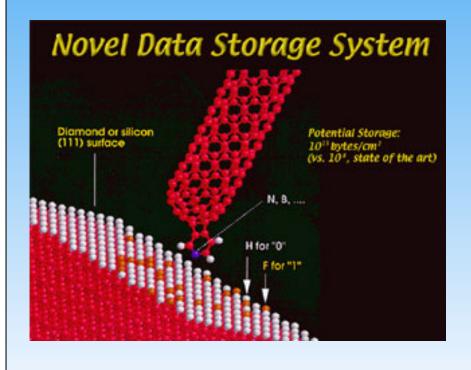


- 1. What novel quantum properties will be enabled by nanostructures (at room temp.)?
- 2. How different from bulk behavior?
- 3. What are the surface reconstructions and rearrangements of atoms in nanocrystals?
- 4. Can carbon nanotubes of specified length and helicity be synthesized as pure species? Heterojunctions in 1-D?
- 5. What new insights can we gain about polymer, biological...systems from the capability to examine single-molecule properties?
- 6. How can one use parallel self-assembly techniques to control relative arrangements of nanoscale components according to predesigned sequence?
- 7. Are there processes leading to economic preparation of nanostructures with control of size, shape... for applications?



### **Impact of Nanotechnology**

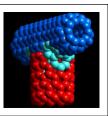




- Computing and Data Storage
- Materials and Manufacturing
- Health and Medicine
- Energy and Environment
- Transportation
- National Security
- Space exploration



# **Nanoelectronics and Computing**

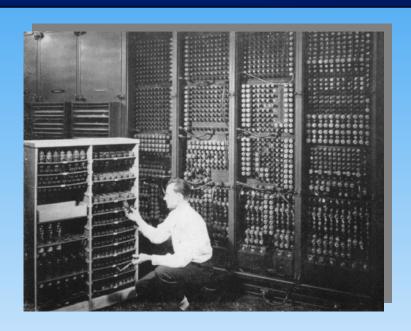


#### **Past**

Shared computing thousands of people sharing a mainframe computer



Present Personal computing



#### Future

Ubiquitous computing thousands of computers sharing each and everyone of us; computers embedded in walls, chairs, clothing, light switches, cars....; characterized by the connection of things in the world with computation.



# Nanoelectronics: What is Expected from Alternative Technologies?

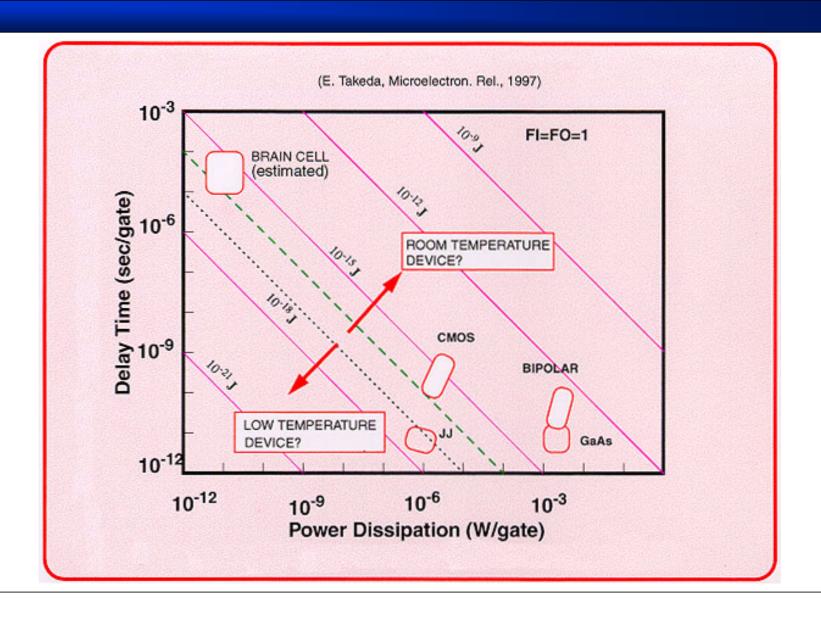


- Must be easier and cheaper to manufacture than CMOS
- Need high current drive; should be able to drive capacitances of interconnects of any length
- High level of integration (>10<sup>10</sup> transistors/circuit)
- High reproducibility (better than ± 5%)
- Reliability (operating time > 10 years)
- Very low cost ( < 1  $\mu$ cent/transistor)
- Everything about the new technology must be compelling and simultaneously further CMOS scaling must become difficult and not cost-effective. Until these two happen together, the enormous infrastructure built around silicon will keep the silicon engine humming....



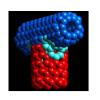
# **Switching Energy of Electron Devices and Brain Cells**







### Materials and Manufacturing



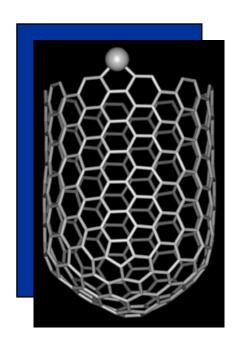
- Ability to synthesize nanoscale building blocks with control on size, composition etc. further assembling into larger structures with designed properties will revolutionize materials manufacturing
  - Manufacturing metals, ceramics, polymers, etc. at exact shapes without machining
  - Lighter, stronger and programmable materials
  - Lower failure rates and reduced life-cycle costs
  - Bio-inspired materials
  - Multifunctional, adaptive materials
  - Self-healing materials
- Challenges ahead
  - Synthesis, large scale processing
  - Making useful, viable composites
  - Multiscale models with predictive capability
  - Analytical instrumentation



# Materials and Manufacturing Some Recent Advances



- Carbon Nanotubes
- Nanostructured Polymers
- Optical fiber preforms through sol-gel processing of nanoparticles
- Nanoparticles in imaging systems
- Nanostructured coatings
- Ceramic nanoparticles for netshapes







Source: IWGN Report



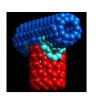
# **Sensors for the Automotive Industry**



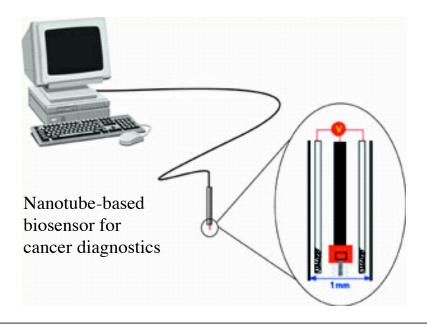
- Automotive electronics to grow to \$30 Billion by 2005
- Pressure to keep cost of devices low is enormous
- Sensors in use now include monitoring wheel speed, pedal positions, oxygen sensors to check exhaust, accelerometers to detect sudden stops, pressure and temperature sensors
- Future systems
  - Collision avoidance
  - Break-by-wire, steer-by-wire systems (slowing the car and guiding electrically instead of manually)
  - Sensor systems when new fuel sources become common
- Challenges
  - High temperature survival of sensors
  - Withstanding mechanical shock, hostile environment
  - Conditions: sever swing in T; variable humidity; road salt; noxious gases;  $f \sim 10$  g;  $\sim 10$  year life-time
- MEMS made it in the airbag. But the car interior is a benign environment. Will MEMS work elsewhere in the car?



### Health and Medicine



- Expanding ability to characterize genetic makeup will revolutionize the specificity of diagnostics and therapeutics
  - Nanodevices can make gene sequencing more efficient
- Effective and less expensive health care using remote and in-vivo devices

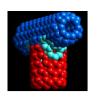




- New formulations and routes for drug delivery, optimal drug usage
- More durable, rejection-resistant artificial tissues and organs
- Sensors for early detection and prevention



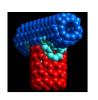
### **Energy and Environment**



- Nanotechnology has the potential to impact energy efficiency, storage and production
- Materials of construction sensing changing conditions and in response altering their inner structure
- Monitoring and remediation of environmental problems; curbing emissions; development of environmental friendly processing technologies
- Some recent examples:
  - Crystalline materials as catalyst support, \$300 b/year
  - Ordered mesoporous material by Mobil oil to remove ultrafine contaminants
  - Nano-particle reinforced polymers to replace metals in automobiles to reduce gasoline consumption



### **National Security**

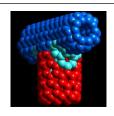


Some critical defense applications of nanotechnology include

- Continued information dominance: collection, transmission, and protection
- High performance, high strength, light weight military platforms while reducing failure rates and life cycle costs
- Chemical/biological/nuclear sensors; homeland protection
- Nano and micromechanical devices for control of nuclear and other defense systems
- Virtual reality systems based on nanoelectronics for effective training
- Increased use of automation and robotics



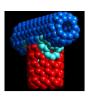
### National Nanotechnology Initiative



- NNI has been effective since FY01. President's request for FY03 \$679 M, representing 17% increase
- Proposal to introduce a Nanotechnology Bill in Congress is at early stages
- "Detection and Protection" gaining importance
- Biggest portion of the funding goes to NSF
  - Followed by DoD, NASA, DOE, NIH
  - All these agencies spend most of their nano funding on university programs
- Very strong activities in Japan, Europe, China, Singapore, fueled by Government Initiatives
- Nano activities in U.S. companies: IBM, Motorola, HP, Lucent, Hitachi USA, Corning, DOW, 3M...
  - In-house R & D
  - Funding ventures
- Nano Centers being established at Universities all across the world
- Emerging small companies
  - VC funding on the increase



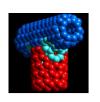
## **Grand Coalition**

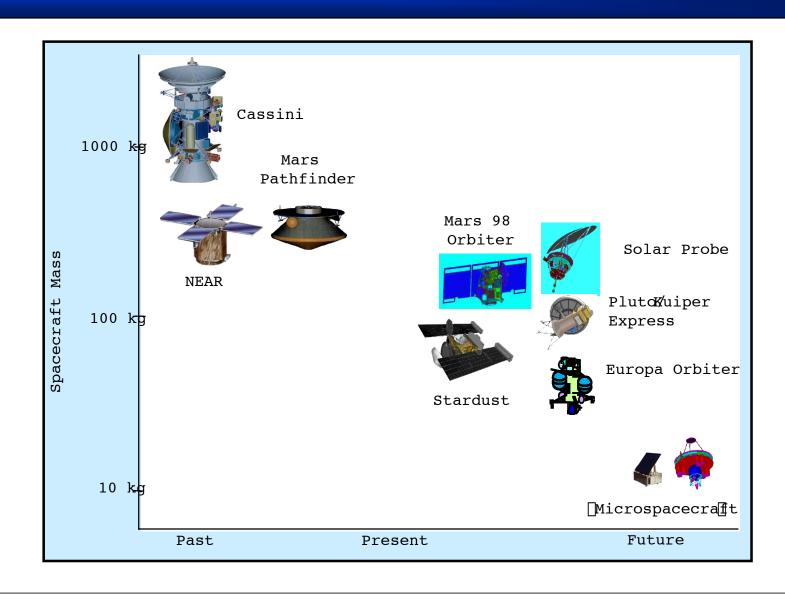


- Academia will play key role in development of nanoscience and technology
  - Promote interdisciplinary work involving multiple departments
  - Develop new educational programs
  - Technology transfer to industry
- Government Labs will conduct mission oriented nanotechnology research
  - Provide large scale facilities and infrastructure for nanotechnology research
  - Technology transfer to industry
- Government Funding Agencies will provide research funding to academia, small business, and industry through the NNI and other programs (SBIR, STIR, ATP...)
- **Industry** will invest only when products are within 3-5 years
  - Maintain in-house research, sponsor precompetitive research
  - Sponsor technology start-ups and spin-offs
- Venture Capital Community will identify ideas with market potential and help to launch start-ups
- **Professional societies** should establish interdisciplinary forum for exchange of information; reach out to international community; offer continuing education courses



### NASA's Own Moore's Law







### Why Nanotechnology at NASA?



- Advanced miniaturization, a key thrust area to enable new science and exploration missions
  - Ultrasmall sensors, power sources, communication, navigation, and propulsion systems with very low mass, volume and power consumption are needed

• Revolutions in electronics and computing will allow reconfigurable,

autonomous, "thinking" spacecraft

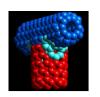
Europa Submarine

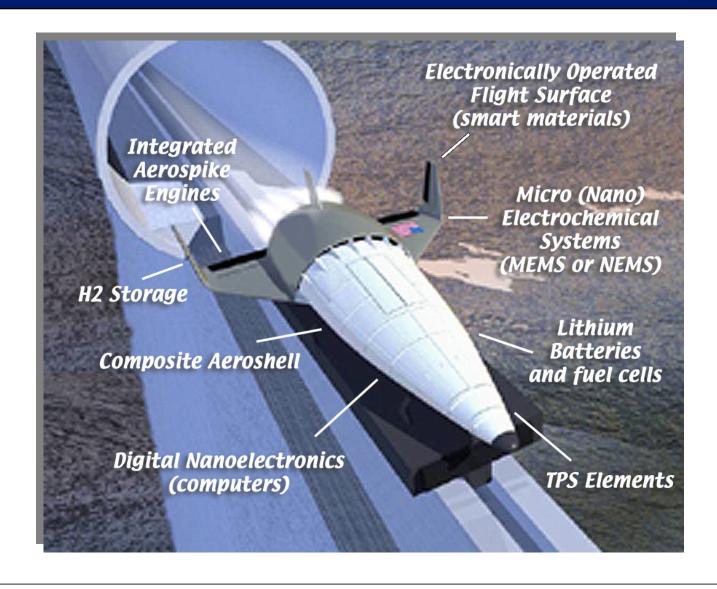
- Nanotechnology presents a whole new spectrum of opportunities to build device components and systems for entirely new space architectures
  - Networks of ultrasmall probes on planetary surfaces
  - Micro-rovers that drive, hop, fly, and burrow
  - Collection of microspacecraft making a variety of measurements





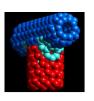
### **Just one Material, so much Potential**







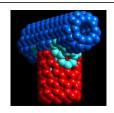
### **NASA's Investments in Nano**



- NASA Ames Center for Nanotechnology, started in 1996, is the largest in-house R & D in Federal Government; consists of 50 scientists and engineers working on various aspects of experimental and computational nanotechnology fields.
- NASA Ames has strong collaboration with the academia
  - undergraduate student research program
  - high school student research program
- Smaller programs at JSC (CNT composites), Langley (Nano materials), Glenn (Energy storage), and JPL
- NASA's university-based Nano-Institutes
  - Three institutes, \$3 M/year/institute for 5 + optional 3 years (Purdue, UCLA, Princeton/Texas A & M)
- Recent spin-off: Integrated Nanosystems, Inc.



### NASA Ames Nanotechnology Research Focus



#### \* Carbon Nanotubes

- Growth (CVD, PECVD)
- Characterization
- AFM tips
  - Metrology
  - Imaging of Mars Analog
  - Imaging Bio samples
- Electrode development
- Biosensor (cancer diagnostics)
- Chemical sensor
- Logic Circuits
- Chemical functionalization
- Gas Absorption
- Device Fabrication

#### \* Molecular Electronics

- Synthesis of organic molecules
- Characterization
- Device fabrication

#### \* Inorganic Nanowires

#### \* Protein Nanotubes

- Synthesis
- Purification
- Application Development

#### \* Genomics

- Nanopores in gene sequencing
- Genechips development

#### \* Computational Nanotechnology

- CNT Mechanical, thermal properties
- CNT Electronic properties
- CNT based devices: physics, design
- CNT based composites, BN nanotubes
- CNT based sensors
- DNA transport
- Transport in nanopores
- Nanowires: transport, thermoelectric effect
- Transport: molecular electronics
- Protein nanotube chemistry

#### \* Quantum Computing

#### Computational Quantum Electronics

- Noneq. Green's Function based Device Simulator
- \* Computational Optoelectronics
- \* Computational Process Modeling



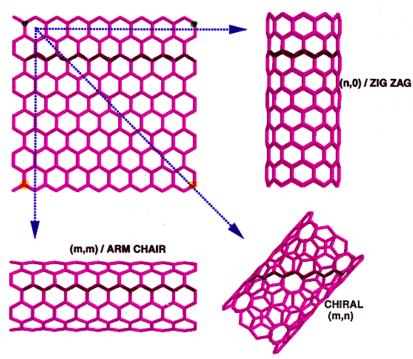
### **Carbon Nanotube**

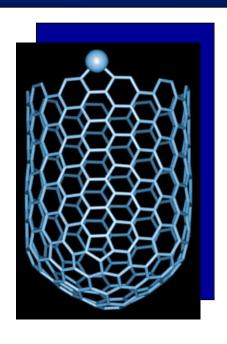


CNT is a tubular form of carbon with diameter as small as 1 nm. Length: few nm to microns.

CNT is configurationally equivalent to a two dimensional graphene sheet rolled into a tube.

STRIP OF A GRAPHENE SHEET ROLLED INTO A TUBE



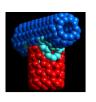


CNT exhibits extraordinary mechanical properties: Young's modulus over 1 Tera Pascal, as stiff as diamond, and tensile strength ~ 200 GPa.

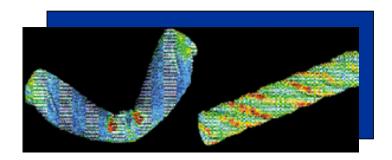
CNT can be metallic or semiconducting, depending on chirality.

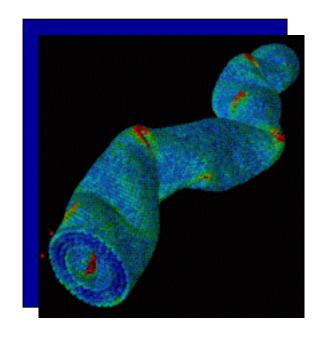


## **CNT Properties**



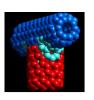
- The strongest and most flexible molecular material because of C-C covalent bonding and seamless hexagonal network architecture
- Young's modulus of over 1 TPa vs 70 GPa for Aluminum, 700 GPA for C-fiber
  - strength to weight ratio 500 time > for Al; similar improvements over steel and titanium; one order of magnitude improvement over graphite/epoxy
- Maximum strain ~10% much higher than any material
- Thermal conductivity ~ 3000 W/mK in the axial direction with small values in the radial direction



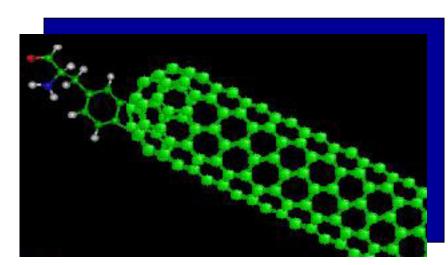




# **CNT Properties (cont.)**



- Electrical conductivity six orders of magnitude higher than copper
- Can be metallic or semiconducting depending on chirality
  - 'tunable' bandgap
  - electronic properties can be tailored through application of external magnetic field, application of mechanical deformation...
- Very high current carrying capacity
- Excellent field emitter; high aspect ratio and small tip radius of curvature are ideal for field emission
- Can be functionalized





### CNT Applications: Structural, Mechanical



- High strength composites
- Cables, tethers, beams
- Multifunctional materials
- Functionalize and use as polymer back bone
  - plastics with enhanced properties like "blow molded steel"
- Heat exchangers, radiators, thermal barriers, cryotanks
- Radiation shielding
- Filter membranes, supports
- Body armor, space suits

### Challenges

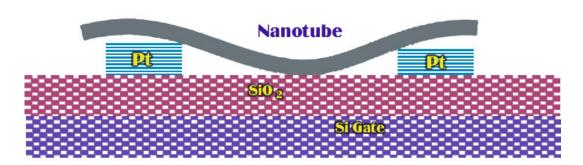
- Control of properties, characterization
- Dispersion of CNT homogeneously in host materials
- Large scale production
- Application development



### **CNT Applications: Electronics**



- CNT quantum wire interconnects
- Diodes and transistors for computing
- Capacitors
- Data Storage
- Field emitters for instrumentation
- Flat panel displays
- THz oscillators



### Challenges

- Control of diameter, chirality
- Doping, contacts
- Novel architectures (not CMOS based!)
- Development of inexpensive manufacturing processes



### CNT Applications: Sensors, NEMS, Bio



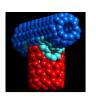
- CNT based microscopy: AFM, STM...
- Nanotube sensors: force, pressure, chemical...
- Biosensors
- Molecular gears, motors, actuators
- Batteries, Fuel Cells: H<sub>2</sub>, Li storage
- Nanoscale reactors, ion channels
- Biomedical
  - in vivo real time crew health monitoring
  - Lab on a chip
  - Drug delivery
  - DNA sequencing
  - Artificial muscles, bone replacement, bionic eye, ear...

#### **Challenges**

- Controlled growth
- Functionalization with probe molecules, robustness
- Integration, signal processing
- Fabrication techniques



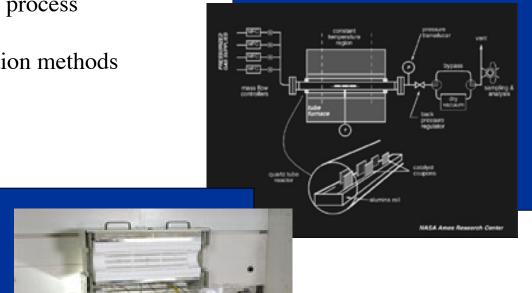
# **CNT Synthesis**



- CNT has been grown by laser ablation (pioneering at Rice) and carbon arc process (NEC, Japan) early 90s.
  - SWNT, high purity, purification methods
- CVD is ideal for patterned growth (electronics, sensor applications)

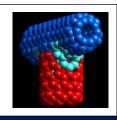
Well known technique from microelectronics

- Hydrocarbon feedstock
- Growth needs catalyst (transition metal)
- Multiwall tubes at 500-800° deg. C.
- Numerous parameters influence CNT growth

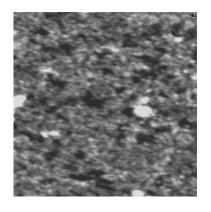


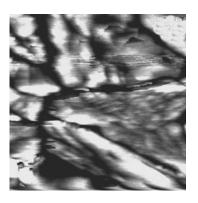


## **Catalyst Characterization**

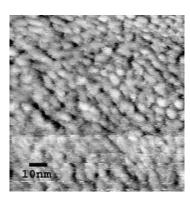


- Catalyst surface characterized by AFM (with SWNT tip) and STM.
- AFM image of as-sputtered 10 nm iron catalyst (area shown is 150 nm x 150 nm). Also, the same surface after heating to 750° C (and cooled) showing Fe particles rearranging into clusters.



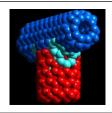


- STM image of a nickel catalyst showing nanoscale particles
- These results are consistent with high resolution TEM showing particles as small as 2 nm.

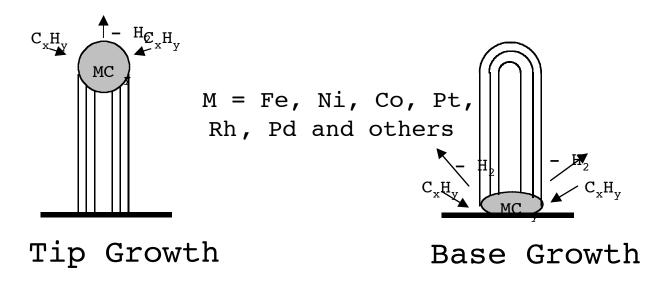




# **CVD Growth Mechanisms For Carbon Nanotubes**



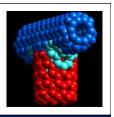
- Adsorption and decomposition of feedstock on the surface of the catalyst particle
- Diffusion of carbon atoms into the particle from the supersaturated surface
- Carbon precipitates into a crystalline tubular form
- Particle remains on the surface and nanotube continues to lengthen "base growth" mechanism
- Growth stops when graphitic overcoat occurs on the growth front "catalytic poisoning"

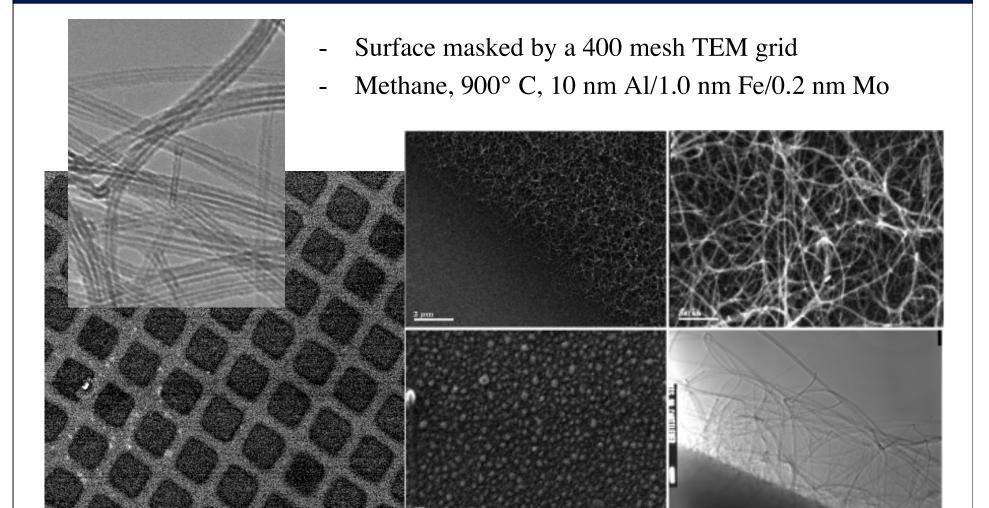


Typically occurs when there are Occurs when the metal-surface very weak metal-surface interactions interactions are strong



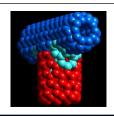
### **SWNTs on Patterned Substrates**

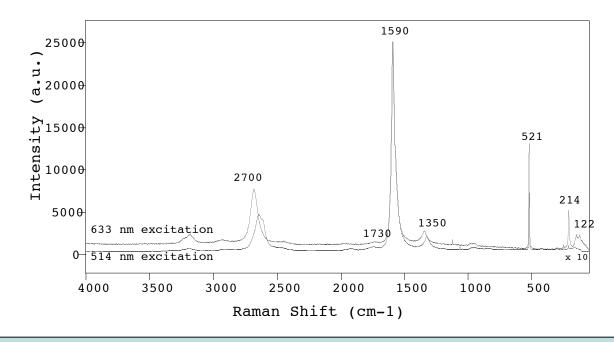






## Raman Analysis of SWNTs

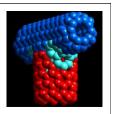




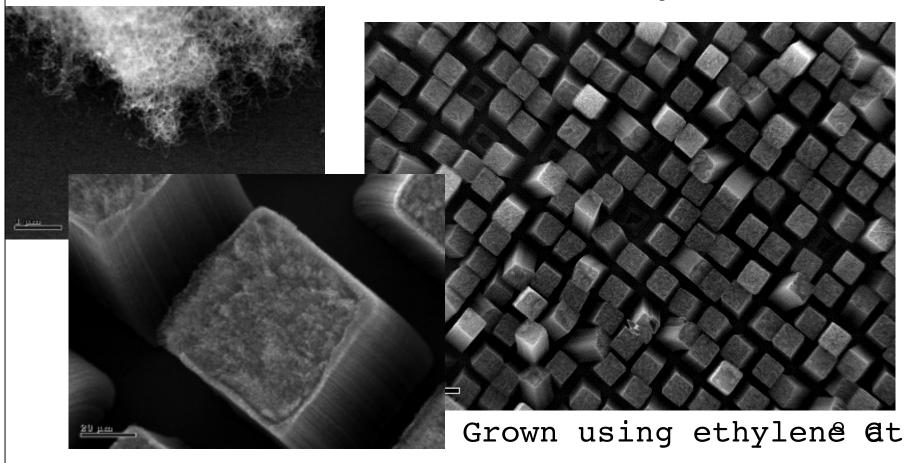
- 2 mw laser power, 1  $\mu$ m focus spot
- Characteristic narrow band at 1590 cm<sup>-1</sup>
- Signature band at 1730 cm<sup>-1</sup> at SWNTs
- Diameter distribution 1.14 nm to 2 nm; consistent with TEM results
- High metallic % of NTs



### **Multiwall Nanotube Towers**



- Surface masked by a 400 mesh TEM grid; 20 nm Al/ 10 nm Fe; nanotubes grown for 10 minutes

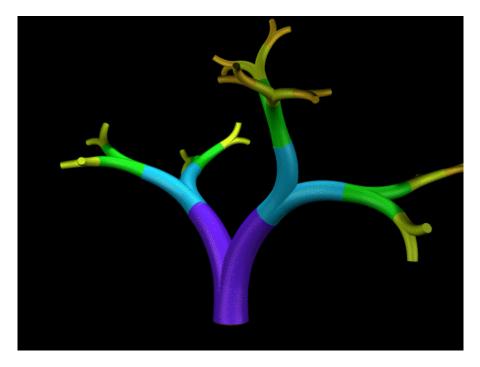


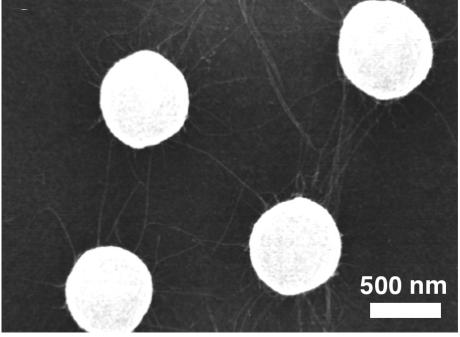


### Four-level CNT Dentritic Neural Tree



- Neural tree with 14 symmetric Y-junctions
- Branching and switching of signals at each junction similar to what happens in biological neural network
- Neural tree can be trained to perform complex switching and computing functions
- Not restricted to only electronic signals; possible to use acoustic, chemical or thermal signals







# **ICP Reactor for CNT Growth**



- Inductively coupled plasmas are the simplest type of plasmas; very efficient in sustaining the plasma; reactor easy to build and simple to operate
- Quartz chamber 10 cm in diameter with a window for sample introduction
- Inductive coil on the upper electrode
- 13.56 MHz independent capacitive power on the bottom electrode
- Heating stage for the bottom electrode

• Operating conditions

 $CH_4/H_2:5-20\%$ 

Total flow: 100 sccm Pressure: 1 - 20 Torr

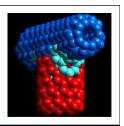
Inductive power: 100-200 W

Bottom electrode power: 0 - 100 W



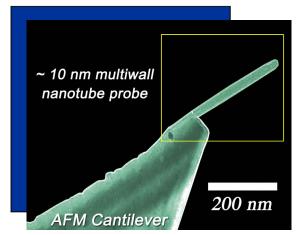


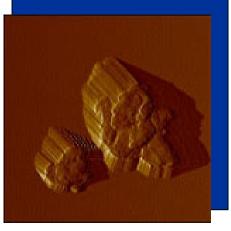
# **CNT in Microscopy**

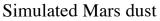


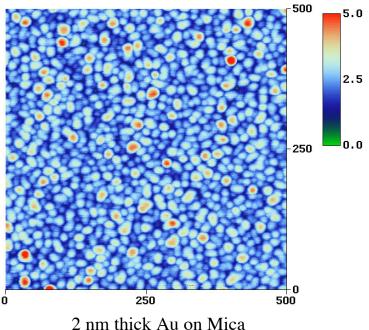
Atomic Force Microscopy is a powerful technique for imaging, nanomanipulation, as platform for sensor work, nanolithography...

Conventional silicon or tungsten tips wear out quickly. CNT tip is robust, offers amazing resolution.











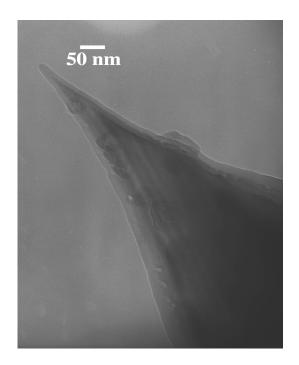
NASA Ames Research Center Ramsey Stevens, Lance Delzeit, Cattien Nguyen

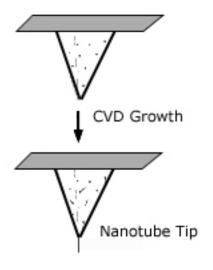


## **Fabrication of CNT Probes**

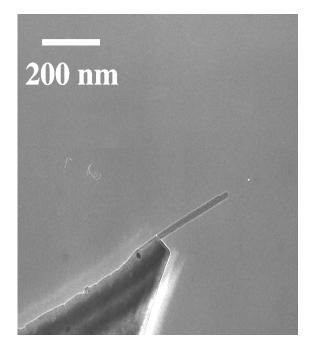


Transition metal catalyst is deposited from liquid phase or sputtered on the tip of the cantilever





Carbon nanotube is grown in thermal CVD or plasma reactor

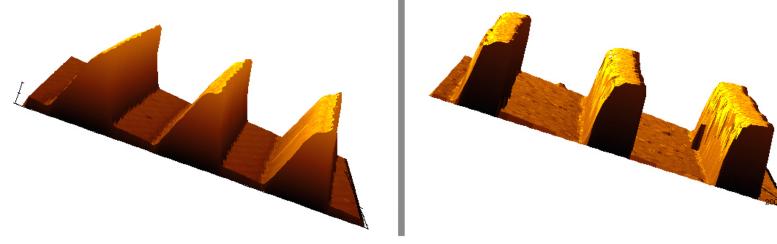


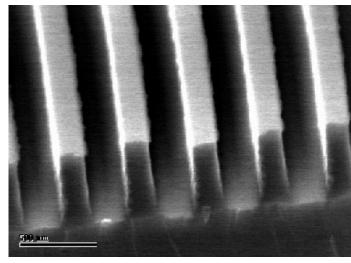


# **Profilometry in Integrated Circuit Manufacturing**



280 nm line/space. Array of polymeric resist on a silicon substrate.

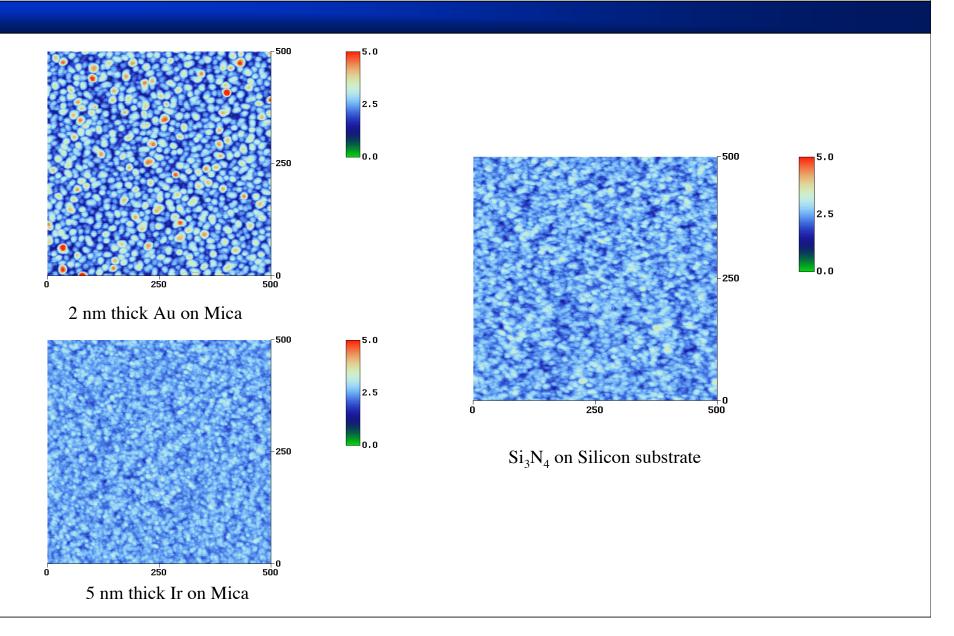






# AFM Imaging with Single Wall Nanotube Tips







## **Imaging of Mars Analogs**

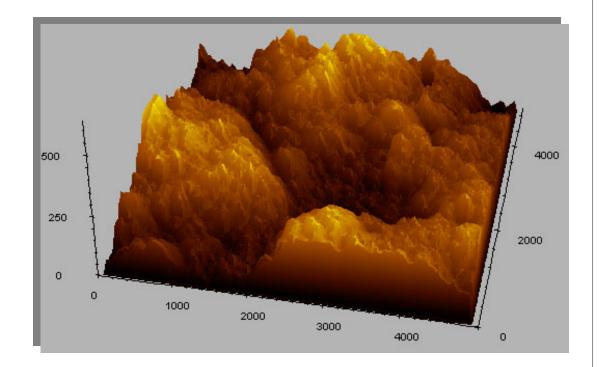




Optical image

AFM image using carbon nanotube tip

Red Dune Sand (Mars Analog)





### **CNT Based Biosensors**

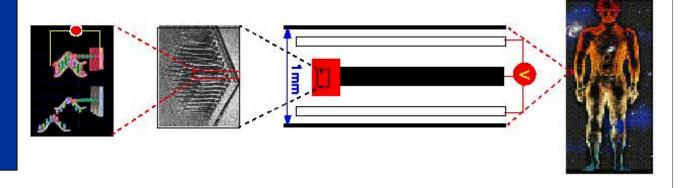


• Our interest is to develop sensors for astrobiology to study origins of life. CNT, though inert, can be functionalized at the tip with a probe molecule. Current study uses AFM as an experimental platform.

- The technology is also being used in collaboration with NCI to develop sensors for cancer diagnostics
  - Identified probe molecule that will serve as signature of leukemia cells, to be attached to CNT
  - Current flow due to hybridization will be through CNT electrode to an IC chip.
  - Prototype biosensors catheter development

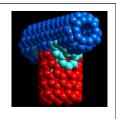


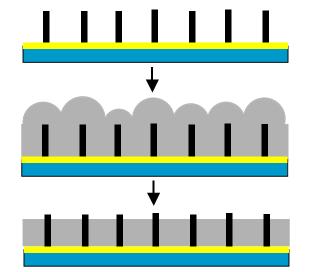
- Direct, fast response
- High sensitivity
- Single molecule and cell signal capture and detection



# Ames Research Center

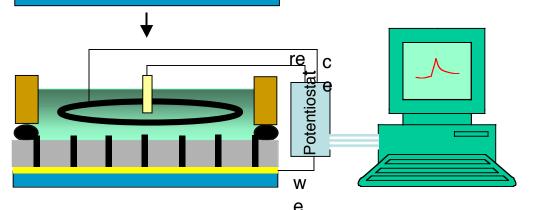
# The Fabrication of CNT Nanoelectrode Array





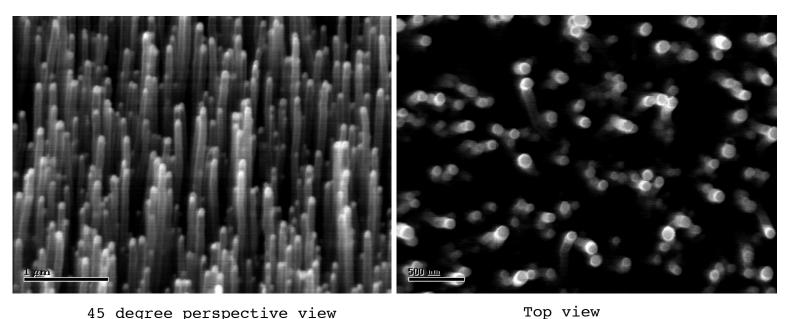
- (1) Growth of Vertically Aligned CNT Array
- (2) Dielectric Encapsulation
- (3) Planarization

(4) Electrical Property Characteriz
By Current-sensing AFM



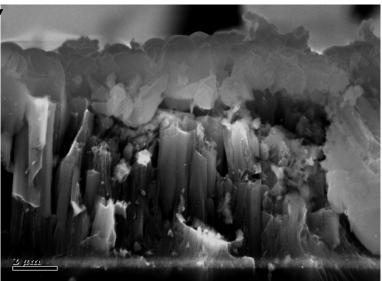
(5) Electrochemical Characterization

#### Fabrication of CNT Nanoelectrodes

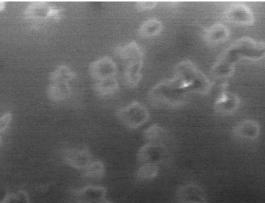


J. Li eAppl, PhysLett81(5) 910 (2002)

45 degree perspective view



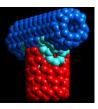
Side view after encapsulation

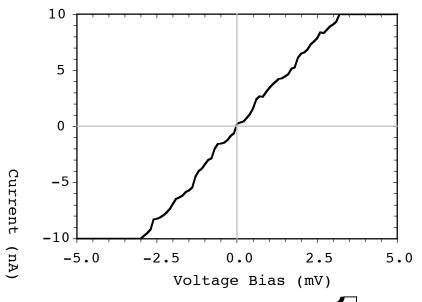


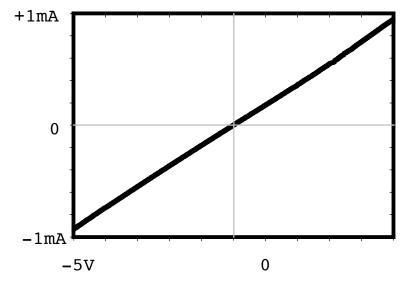
Top view after planarization

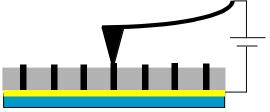


#### Electrical Properties of CNT









HP analyzer

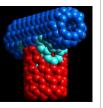
**Current Sensing AFM** 

Four-probe station

And HP parameter analyzer



#### Chemical Functionalization



$$CO_{2}H \xrightarrow{iPr_{2}NEt} CO_{2}$$

$$Cy-N=C=N-Cy$$

$$HO^{-N}$$

$$O$$

$$H_{2}N$$

$$FC$$

$$FC$$

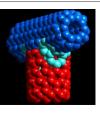
$$FC$$

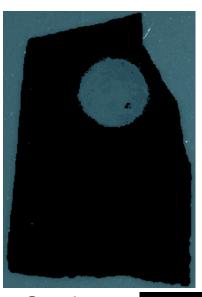
$$FC$$

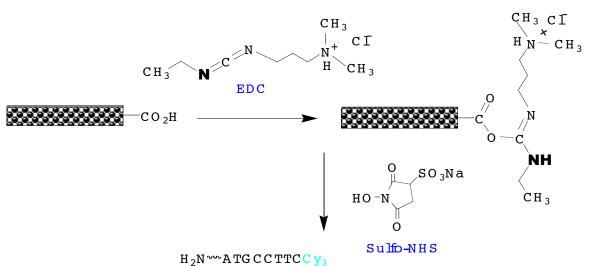
Highly selective reaction of primary amine with surface -COOH group



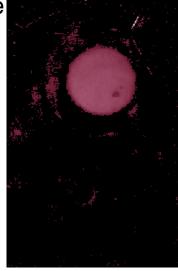
#### Functionalization of DNA



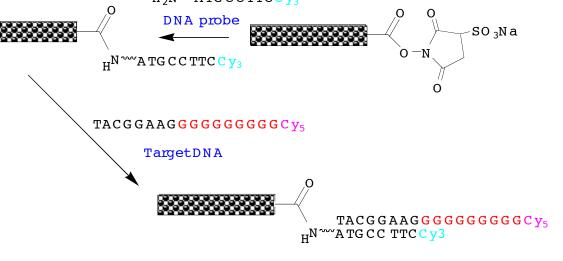




Cy3 image

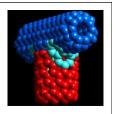


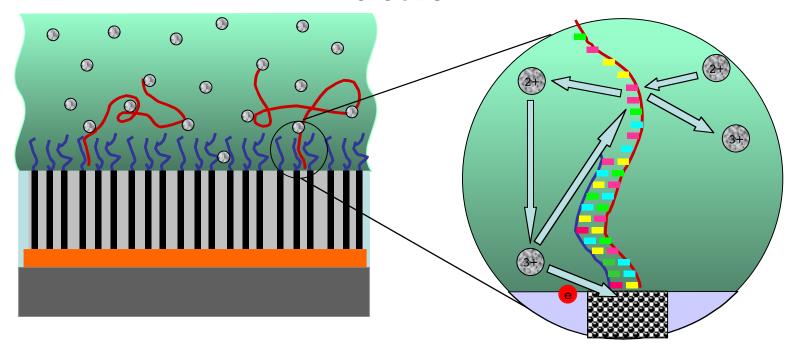
Cy5 image





# CNT DNA Sensor Using Electrochemical Detection



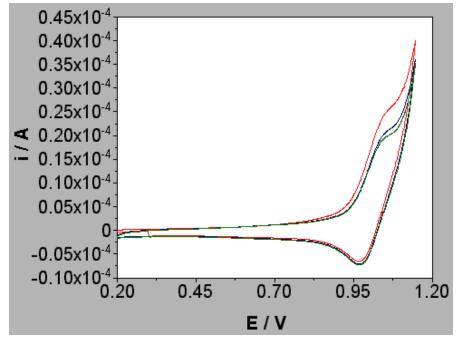


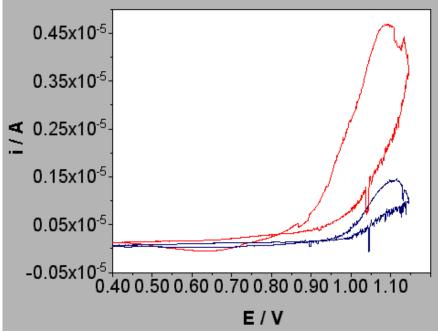
- MWNT array electrode functionalized with DNA/PNA probe as an ultrasensitive sensor for detecting the hybridization of target DNA/RNA from the sample.
  - Signal from redox bases in the excess DNA single strands
- The signal can be amplified with metal ion mediator  $\left[Ru(bPy)_3^{2+}\right]$  oxidation catalyzed by Guanine.



# Electrochemical Detection of DNA Hybridization



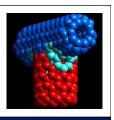




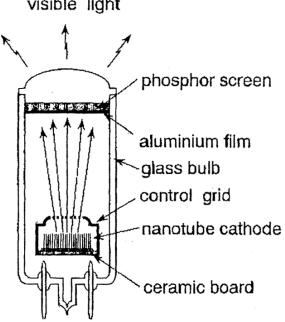
 $1^{st}$ ,  $2^{nd}$ , and  $3^{rd}$  cycle in cyclic voltammetry  $1^{st} - 2^{nd}$  scan: mainly DNA signal  $2^{nd} - 3^{rd}$  scan: Background



## **CNT - Field Emission Devices**

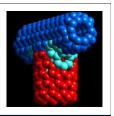


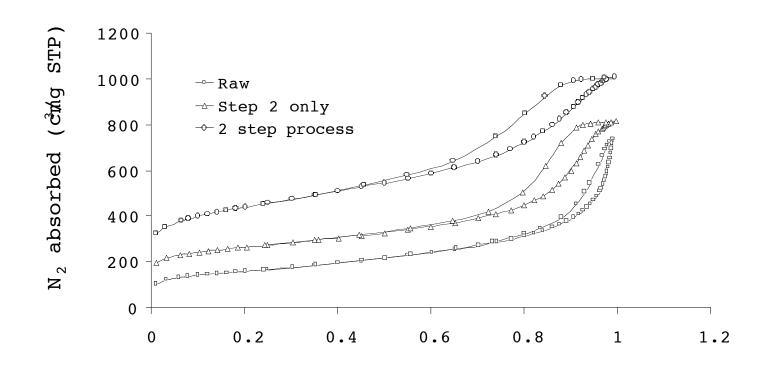
- When subjected to high E field, electrons near the Fermi level can overcome the energy barrier to escape to the vacuum level
- Fowler Nordheim equation:  $I = aV^2 \exp(-b\phi^{1.5}/\beta V)$
- Critical: low threshold E field, high current density, high emission site density (for high resolution displays)
- Tips: Mo, Si, diamond
- Applications:
  - Cathode ray lighting elements
  - Flat panel displays
  - Gas discharge tubes in telecom networks





# N<sub>2</sub> Adsorption Isotherm





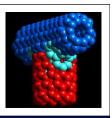
• Estimated surface area of purified HiPCo SWNTs is 1580 m<sup>2</sup>/gm

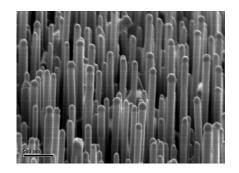
Relative Pressure (P/Po)

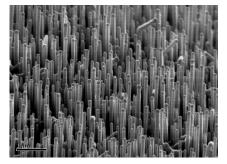
• Applications in catalysis, gas absorption....

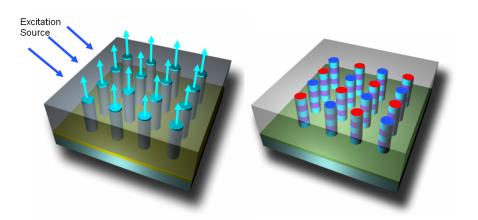


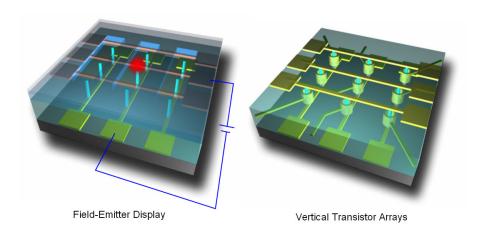
## **Zinc Oxide Nanowires**

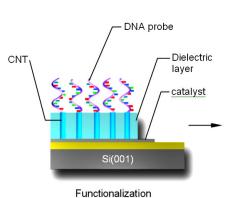


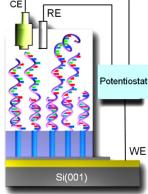












Detection

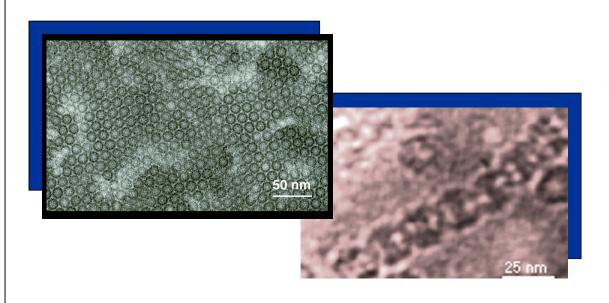


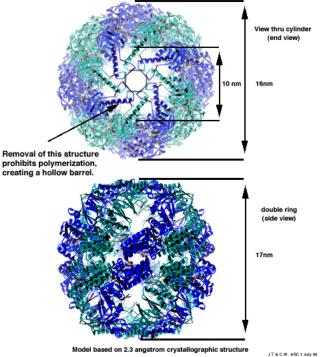
### **Protein Nanotubes**



• Heat shock protein (HSP 60) in organisms living at high temperatures ("extremophiles") is of interest in astrobiology

• HSP 60 can be purified from cells as a double-ring structure consisting of 16-18 subunits. The double rings can be induced to self-assemble into nanotubes.







# Extremophile Proteins for Nano-scale Substrate Patterning



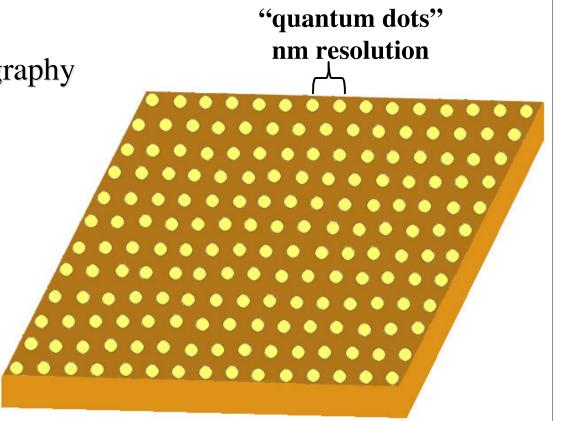
#### Nano-scale engineering for high resolution lithography

Future: Bio-based lithography

•Batch self-assembly

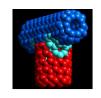
Evolving

Inexpensive



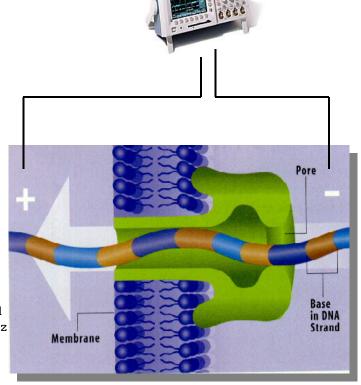


### **DNA Sequencing with Nanopores**



The Concept

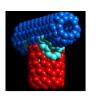
- Nanopore in membrane (~2nm diameter)
- DNA in buffer
- Voltage clamp
- Measure current

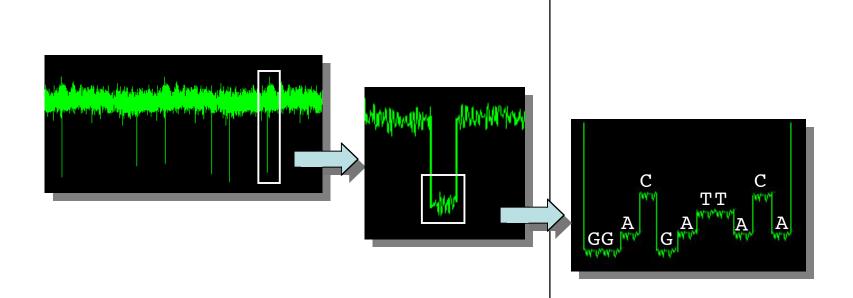


G. Church, Eduanton J. Golovchenktarvard
D. Deamer, UC Santa Cruz



#### **The Sequencing Concept**



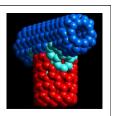


Present

Future



### **Undergraduate Engineering Curriculum**



Before taking the bread and butter courses, the undergraduate training begins with:

**NOW** 

#### SHOULD WE CONSIDER?







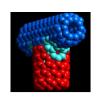
## **Undergraduate Curriculum**



- Should elective courses on nanotechnology be considered (one or two)? If so, coverage includes, but not limited to:
  - Bulk vs. nano properties
  - Introduction to synthesis and characterization
  - Examples of nanomaterials: tubes, wires, particles...
  - Surface phenomena
  - Quantum phenomena
  - Focus on emerging applications
  - ?
- Summer internship and/or academic year co-op
  - National labs
  - Small and large companies with nano programs
  - University research
- Degree in Nanotechnology?
  - Flinders University and University of New South Wales in Australia now offer B. Sc. in Nanoscience and Technology
  - Leeds University and Crane University in U.K. offer M. Sc. in Nanoscience and Technology
  - This, of course, has to be a university-wide effort with courses taught by Physical and Biological Sciences and **Engineering** Departments







- Nanotechnology is an enabling technology that will impact electronics and computing, materials and manufacturing, energy, transportation....
- The field is interdisciplinary but everything starts with material science. Challenges include:
  - Novel synthesis techniques
  - Characterization of nanoscale properties
  - Large scale production of materials
  - Application development
- Opportunities and rewards are great and hence, tremendous worldwide interest
- Integration of this emerging field into engineering and science curriculum is important to prepare the future generation of scientists and engineers